Compilation of Preliminary Data Analyses for the Big Bend Regional Aerosol and Visibility Observational (BRAVO) Study

BRAVO Technical Committee
April 2, 2002

Note: This is a compilation of independent data analyses performed to date; the authors' conclusions do not necessarily represent the views of the BRAVO Technical Committee.

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Introduction

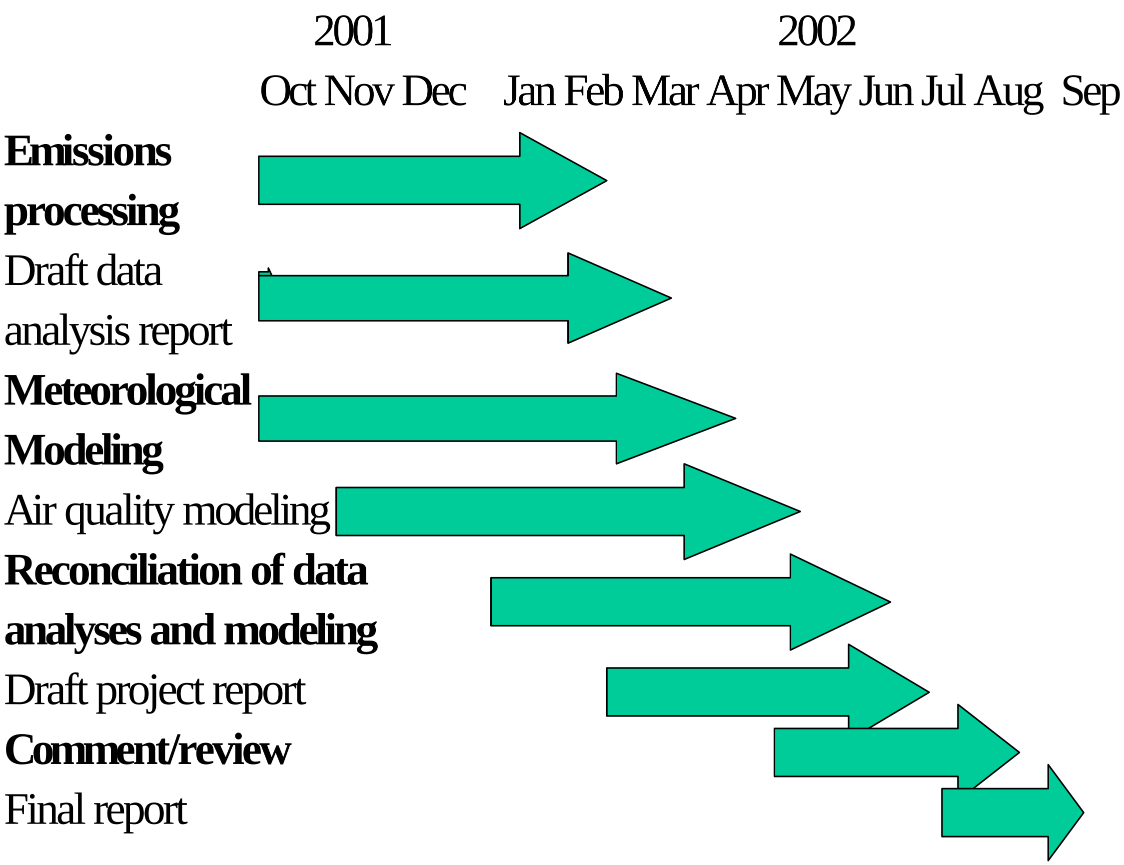
The Big Bend Regional Aerosol and Visibility Observational (BRAVO) Study is a multi-year analysis of the causes for increased haze in the vicinity of Big Bend National Park, Texas. The BRAVO Study was funded by the U.S. Environmental Protection Agency (EPA) and the U.S. National Park Service (NPS). It is overseen by a Steering Committee consisting of representatives of EPA, NPS, and the Texas Natural Resource Conservation Commission (TNRCC). A Technical Committee conceived and implemented the field study and is overseeing the subsequent data analyses and regional air quality modeling. A Non-governmental Organization (NGO) Committee, consisting of industry and environmental group representatives, participates in BRAVO meetings.

The major goal of BRAVO is to identify the source regions and source types responsible for the haze at Big Bend National Park. Because of the Park's location on the U.S.-Mexico border, it was surmised that emissions from both countries contributed to the haze, but the degree of impact due to such source regions and types was unknown. The program plan for the BRAVO Study is detailed in Green et al. (2000) and provides more detail about individual project components.

The BRAVO field study was completed October 31, 1999. Since that time, analyses have proceeded, including those for filters collected during the study, meteorological data, and emissions data. The purpose of this draft compilation report is to provide a general update of current knowledge acquired through the data analyses thus far completed. Neither this draft report nor the papers informally referenced herein should be considered final conclusions. In some cases the results are somewhat contradictory. This is to be expected as the Technical Committee debates the, at times, ambiguous meanings of the results and reaches consensus on reasonable conclusions. This report does not address the regional air quality modeling which is currently in-progress. Figure 1 illustrates the next steps in BRAVO, culminating in a final project report by late 2002.

This draft compilation report includes a "Summary of Data Analyses" section, briefly highlighting some of the recent, technical papers given by members of the BRAVO Technical Committee. For purposes of discussion, the papers are divided into four categories: Emissions, atmospheric tracers, particles, and source attribution. A second section consists of a comprehensive tabulation of on-going and expected BRAVO research compiled by Dr. Ivar Tombach, a member of the BRAVO Technical Committee.

BRAVO COMPLETION SCHEDULE



Summary of Data Analyses

Emissions

Dr. Hampden Kuhns of Desert Research Institute (DRI) was the author of the BRAVO emissions inventory, which is an essential input to regional air quality modeling and determination of source type impacts at Big Bend. The BRAVO emissions inventory acquired emissions data for carbon monoxide (CO), ammonia (NH_3), nitrogen oxides (NO_x), coarse particulate matter (PM_{10}), fine particulate matter ($PM_{2.5}$), sulfur dioxide (SO_2), and volatile organic compounds (VOC). BRAVO focused on obtaining emissions totals from 14 U.S. States and 10 Mexican States.

On average, sulfates, which result from SO_2 emissions, account for almost half of the visibility impairment at the Park and, thus, are the largest contributor. It is interesting to note that within the 14 U.S. States and 10 Mexican States that are highlighted in the BRAVO emissions inventory are 5.8 million tons/year and 2.6 million tons/year of SO_2 emissions, respectively. Although the U.S. totals are considerably larger, the Mexican totals represent a sizable 31% of total SO_2 emissions within this emphasis area.

Geographically speaking, Dr. Kuhns' work shows that the Big Bend area is not so much isolated from pollutant emissions as it is surrounded by such emissions.

Atmospheric tracers

Synthetic atmospheric tracers are unique, inert chemical compounds that can be released into the atmosphere and then sampled along the path to, and at, the receptor point of interest. A tracer arriving at a particular impact point indicates that winds carried pollutant emissions from the release point to the impact point, but cannot indicate the concentration of pollutant at the impact point due to chemical transformation and deposition of the pollutant enroute.

In the case of BRAVO, tracers were released from July through October 1999 at Big Brown power plant approximately 100 miles southeast of Dallas, at the Parish power plant near Houston, at San Antonio to represent urban emissions, and at Eagle Pass, which was the closest U.S. point to the Carbon 1-2 power plants in Mexico. It is important to note that TXU Energy and Reliant Power, owners of the Big Brown and Parish Power Plants, respectively, volunteered to release atmospheric tracers from their plants in the interest of scientifically determining the source regions and source types that are important to haze at the Park. Samplers collected the tracers at 20 different locations throughout Texas and in Oklahoma, including at Big Bend National Park.

In their paper, Dr. Marc Pitchford of the U.S. National Oceanic and Atmospheric Administration and colleagues at DRI, U.S. Department of Energy-Brookhaven National Laboratory (BNL), and NOAA reported that tracers released from each of the four sites were registered by samplers at Big Bend National Park. The percentage of observations of the tracers at the various points in the Park varied from 16-33% for the tracer released at Eagle Pass to 1-10% for the tracer released at the Big Brown power plant.

Tracers can be used not only to determine if an air parcel arrives at the impact point but also to categorize impacts based on emissions release timing. In a paper by Dr. Warren White of Washington University and colleagues from NOAA, DRI, and BNL, results from the "timing tracers" at Eagle Pass were discussed. These tracers seem to indicate an average travel time of an air parcel of approximately 15 hours from Eagle Pass to the Park.

Particles

In order to accurately estimate the origins of the aerosol fine particulate matter that constitute the bulk of visibility degradation at Big Bend National Park, one has to characterize the aerosols. A large part of the BRAVO analytical work to date has focused on this task.

Dr. Lowell Ashbaugh and colleagues of the University of California-Davis (UCD) and at DRI have analyzed temporal and spatial characteristics of the particle types during the field study and have found source regions for particles at the Park to be in Texas, outside Texas in the U.S. and in Mexico.

Dr. William Malm of NPS and colleagues at Colorado State University (CSU) have found that light extinction - the root cause of visibility degradation - is due to fine particle scattering (60% of the extinction), water associated with aerosols (14% of extinction), and absorption (8% of extinction).

Dr. Suzanne Herring and colleagues at Aerosol Dynamics, Inc., Air Resource Specialists, Inc., and Rupprecht and Patashnick, Inc. deployed and operated a continuous sulfate monitor at the Park. They concluded that sulfates were a large part of the fine particulate aerosol at the Park during the study period and that there were several days where sulfate maxima at night were well correlated with higher levels of sulfur dioxide. This correlation suggests that, at least for those nighttime periods, the source of much of the sulfate pollution may be relatively near the Park.

Dr. Jeffrey Collett and colleagues at CSU found during the study that daily average sulfate and ammonium ion concentrations at the Park were strongly correlated. The aerosol was found to be acidic most of the time, with ammonium and sulfate located predominantly in submicron aerosol particles and nitrate found in coarse, supermicron particles. They also found that air parcel back trajectories indicate highest sulfate ion concentrations at the Park occurred when parcels had passed over the Texas-Mexico border area, east Texas, and over the States east of Texas.

Dr. Pierre Herckes and colleagues at CSU analyzed the organic portion of the aerosol collected at the Park and found that wood smoke, vehicular exhaust, and smoke from meat cooking are all small contributors to the organic portion. They also found that there was a small biogenic influence and large anthropogenic influence on primary carbonaceous aerosol particles in July through September 1999, but biogenic sources were more dominant in October. This could be due to a seasonal change in wind directions. Also, they concluded that the major portion of the organic aerosol is secondary in origin.

Dr. Jenny Hand and colleagues at CSU and NPS found that at the Park coarse particles (with diameters averaging approximately 3 microns) were dominated by Saharan dust in July and August. Episodes with higher fine soil compositions during this period were linked to Saharan dust events. Smaller diameter aerosols (volume median diameter averaging .26 microns over the study) were apparently dominated by secondary particles from east Texas, the eastern U.S. and the Texas-Mexico border area. They also found that 50% of the fine particulate mass concentration at the Park was due to sulfates, 20% due to soil, 20% due to organic carbon, 4% due to sodium nitrate, and 3% due to elemental carbon.

Source Attribution

Determining the origin of the pollutants responsible for haze at Big Bend National Park is the major function of BRAVO. One of the important steps in identifying the source regions and source types responsible for the haze-producing pollutants is to use statistical and meteorological tools to gain insights into geographic areas of emissions. This work will serve as a complement to future regional air quality modeling analyses.

Ms. Kristi Gebhart and colleagues at NPS, CSU, and UCD used Empirical Orthogonal Function analysis to indicate transport patterns and source areas contributing to measured concentrations in the study area. Highest average sulfur concentrations during BRAVO were in northeast Texas, lower towards the southwest, except an area near the Carbon 1-2 plants where there was a local maximum; the four dominant spatial patterns indicate sources of sulfur in northeast Texas and areas to the northeast as well as the Texas Gulf Coast and the Carbon 1-2 plants. Spatial and temporal patterns of iron as a surrogate for fine soil indicate Saharan dust during the summer, and patterns in selenium indicate primary sources of this endemic tracer, previously linked to coal-burning, are mainly in Texas and to the east. Vanadium is most likely primarily from Mexico. Overall, results suggest unique sources for different aerosol species and show that transport patterns are seasonal with more transport from Mexico to Texas during the summer and more transport from the east and northeast during the fall.

Dr. Bret Schichtel of CSU and Ms. Kristi Gebhart of NPS used airmass histories to examine transport direction, speeds, and heights of mixed layers of the atmosphere which are associated with high and low particulate sulfur concentrations at Big Bend National Park. The researchers found that high sulfur at the Park is primarily associated with prior airmass transport over northeast Mexico, eastern Texas and/or the Southeastern U.S. (Figure 2).

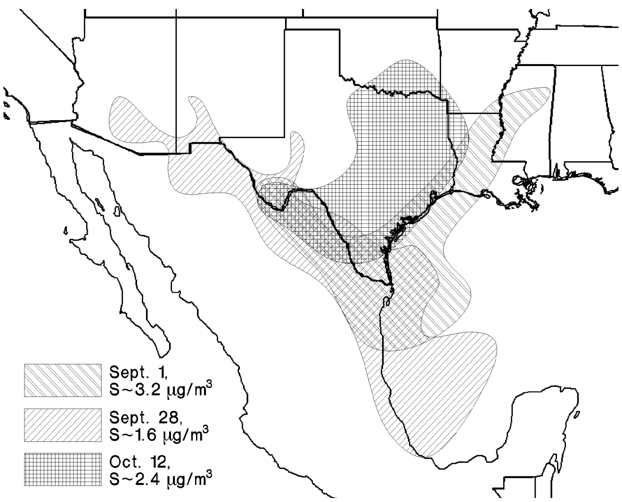


Figure 2. Airmass transport patterns to Big Bend National Park during three sulfur episodes. Each shaded region shows the most likely pathway the airmass traversed prior to impacting the Park.

Low level and low speed transport tended to occur over these regions which is conducive to the accumulation of any emissions in the airmass. The highest Big Bend sulfur concentrations occurred when transport over several of these regions coincided. Based upon their research, Schichtel and Gebhart conclude that east Texas, northeast Mexico, and the U.S. Southeast are potential, prime source areas for sulfur particulate pollution at Big Bend National Park.
Dr. Mark Green of DRI used a technique called TAGIT to attribute particulate sulfur, SO2, and total sulfur at five six-hour sampling sites due to the Eagle Pass tracer. His results showed that SO2 concentrations at Big Bend National Park are probably more locally influenced, while particulate sulfur is probably more regionally influenced. Green also concluded that Carbon 1-2 contribute sizably to SO2 at the Park but probably not more than approximately 10% to particulate sulfur. However, this 10% influence is probably the highest contribution of any single source. He also concluded that TAGIT suggests the Carbon 1-2 SO2 emissions total of

241,000 tons/year may be sizably overestimated.

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Two preliminary studies examined the accuracy of modeling tools in assessing source impacts at the Park. Ms. Kristi Gebhart of NPS and Dr. Bret Schichtel of CSU found that applying "back trajectory" models can involve errors in directional bias in trajectories, and direction and mixing height differences from input meteorological data. Dr. Christian Seigneur and colleagues at Atmospheric and Environmental Research and EPRI used the CMAQ air quality model to simulate inert tracer dispersion during the BRAVO field study. The results of the CMAQ model simulations will be compared later with actual tracer concentrations. These tracer concentrations are currently sequestered until all models have been run to allow a truly objective assessment of model performance.

Finally, in a screening analysis using historical meteorological data and aimed at assessing possible impacts from various source regions, Dr. Naresh Kumar of EPRI used the SCICHEM model with July-October 1990 meteorology. He found that for September 1990 conditions, the maximum SO2 concentrations at Big Bend National Park due to all east Texas power plants was approximately 1 ug/m3. The maximum SO2 concentration due to Carbon 1-2 was greater than 5 ug/m3. For July 1990, the maximum SO2 from all east Texas power plants was less than 0.2 ug/m3, while the maximum impact from Carbon 1-2 was approximately 3 ug/m3. Kumar's study did not factor in oxidation of the SO2 to sulfates and should therefore be considered preliminary and a screening study.

Conclusions

It is important to note that at this stage, any stated conclusions are tentative and may be modified upon the completion of other analyses. With that proviso, these initial data analyses appear to largely support the indications from a preliminary Big Bend regional visibility report (Big Bend Air Quality Work Group, 1999) that both Mexico and Texas sources are impacting haze at Big Bend National Park. Perhaps two of the most noteworthy of the tentative findings thus far are that (1) while it appears Big Bend's haze is due to contributions from sources in a large domain including parts of the U.S. and Mexico, the Carbon 1-2 power plants are perhaps the largest single contributor and (2) sources outside Texas in the U.S. may be impacting the Park in a more sizable way than previously thought. Several researchers have presented information suggesting large coal-fired power plants and other industrial sources to the east of Texas, particularly in the Southeast U.S., are sizable contributors to the haze. Confirming this notion and determining the proportional impacts of the various contributing source regions and source types will be prime goals for a successful study completion.

Bibliography

Big Bend Air Quality Work Group. January 7, 1999. Big Bend National Park Regional Visibility Preliminary Study. 413 pp.

Green, M., H. Kuhns, V. Etyemezian, and M. Pitchford, 2000. Final Program Plan for the Big Bend Regional Aerosol and Visibility Observational Study (BRAVO). 89 pp.

Tabulation of Ongoing and Planned BRAVO Research

Dr. Ivar Tombach has compiled a comprehensive list of BRAVO researchers and their topics. This is presented below to indicate the extent of investigations that will ultimately be included in a BRAVO project report.

BRAVO DATA ANALYSES SUMMARY

Description	Principal Investigator(s)	Planned Completion of Analyses	Means of Communicating Results
Measurements and Data Analyses			
Analyze temporal and spatial characteristics of aerosols, including synoptic meteorological patterns of episodes	Lowell Ashbaugh Crocker Nuclear Laboratory University of California at Davis 530 752-2848 ashbaugh@crocker.ucdavis.edu	October 2001	Results presented in part on BRAVO conference calls 1/25/01, 2/8/01 and 5/31/01. Paper at A&WMA/AGU visibility conference, October 2001. Submit journal manuscript, October 2001.

Analyze ultrafine particles, 0.09 to 0.24 µm, in 6-hr increments by synchrotron XRF, for use in tracking aerosol sources	Thomas Cahill and Steve Cliff Department of Applied Science University of California at Davis 530 752-4674 tacahill@ucdavis.edu	October 2001	Submit paper to *AS&T*, fall 2001. Contribution to BRAVO final report, 2002.
Source profiles for selected sources in Texas	Judy Chow and John Watson Desert Research Institute (Reno) 775 674-7050 judyc@dri.edu	Winter 2002	Presentation to steering committee. Contribution to BRAVO final report, 2002.
Analyze ionic composition of $PM_{2.5}$ and size-resolved aerosol collected at the K-Bar site	Jeff Collett and Sonia Kreidenweis Atmospheric Science Department Colorado State University 970 491-8697 collett@lamar.colostate.edu	September 2001	Results presented in part at BRAVO meeting in August 2000 and conference call 12/7/00. Presentation made at AAAR meeting, November 2000. Paper at A&WMA/AGU visibility conference, October 2001. Submit journal manuscript, fall 2001 Contribution to BRAVO final report in 2002.
Analyze organic composition of $PM_{2.5}$ collected at the K-Bar site	Steven Brown, Jeff Collett and Sonia Kreidenweis Atmospheric Science Department Colorado State University 970 491-8697 collett@lamar.colostate.edu	Fall 2001	Presentation at BRAVO meeting in Sept. 2001. Paper at A&WMA/AGU visibility conference, October 2001. Presentation at AAAR meeting in Nov. 2001. Submit manuscript to *Atmospheric Environment*, February 2002. Contribution to BRAVO final report, 2002.
Analyze aerosol growth vs. RH. Compare nephelometer measurements with results from various thermodynamic models and Tang's growth curves.	Derek Day NPS/CIRA Colorado State University Phone 970 491-8448 Day@CIRA.colostate.edu	September 2001	Paper at A&WMA/AGU visibility conference in October 2001. Presentation at AAAR meeting in Oct. 2001. Submit journal manuscript, November 2001
Evaluation of representativeness of the BRAVO study period	Mark Green Desert Research Institute (LV) 702 895-0445 green@dri.edu	Winter 2002	Presentation to steering committee. Submit journal manuscript. Contribution to BRAVO final report, 2002.
Evaluate representativeness of the measurements and findings of BRAVO	Ivar Tombach 805 388-2341 itombach@aol.com	Spring 2002	Report on analysis. Presentation to steering committee. Contribution to BRAVO final report, 2002

Evaluation of representativeness of meteorology during the BRAVO study period	Bethany Georgoulias, Stuart Dattner TNRCC bgeorgou@tnrcc.state.tx.us sdattner@tnrcc.state.tx.us	Winter 2002	Contribution to BRAVO final report, 2002
Aerosol size distribution measurements	Jennifer Hand, Sonia Kreidenweis and Jeff Collett Atmospheric Science Department Colorado State University 970 491-8350 soniak@aerosol.atmos.colostate.edu	Winter 2002	Present partial results at BRAVO meeting in August 2000 and on conference call, 12/7/00. Presentations at Visibility, Aerosols, and Atmospheric Optics conference, Sept. 2000; AAAR meeting, November 2000; meeting of International Assoc. of Meteorology and Atmospheric Sciences, July 2001. Paper at A&WMA/AGU visibility conference in October 2001. Submit manuscript to *Atmospheric Environment*, February 2002. Contribution to BRAVO final report, 2002.
Estimate the hygroscopicity of aerosol species at Big Bend	Bill Malm, Derek Day, Sonia Kreidenweis, and Jenny Hand NPS/CIRA Colorado State University 970 491-8292 Malm@cira.colostate.edu	Completed	Paper at A&WMA/AGU visibility conference, October 2001.

Description of physical, chemical, and optical properties of fine and coarse particles at Big Bend	Bill Malm, Derek Day, Sonia Kreidenweis, Taehyoung Lee, and Jeff Collett NPS/CIRA Colorado State University 970 491-8292 malrm@cira.colostate.edu	Completed	Paper at A&WMA/AGU visibility conference, October 2001.
Light absorption measurements	Pat Arnott and Hans Moosmüller Desert Research Institute (Reno) 775 674-7023 pat@dri.edu	Completed	Submit article to *Journal of Geophysical Research*, February 2002.
Description of methods, performance, and results of perfluorocarbon tracer release and monitoring.	Marc Pitchford, Mark Green, Hampden Kuhns, Vic Etyemezian, Russell Dietz, and Tom Watson Desert Research Institute (LV) 702 895-0432 marcp@dri.edu	Overview completed. More complete description October 2001	Paper at A&WMA/AGU visibility conference, October 2001. Section for BRAVO final report, 2002. Submit journal article.
Preliminary analysis of perfluorocarbon tracer measurements	Warren White, Russell Dietz, Mark Green, Marc Pitchford, and Thomas Watson Washington University 314 726-6941 white@wuchem.wustl.edu	Winter 2002	Paper at A&WMA/AGU visibility conference, October 2001.
Trend Analysis of Visibility Data from BRAVO	Bethany Georgoulias, Stuart Dattner TNRCC bgeorgou@tnrcc.state.tx.us sdattner@tnrcc.state.tx.us	March 2002	TNRCC Report Contribution to BRAVO final report, 2002 Conference and/or Journal

Spatial and Temporal Analysis of Aerosol Data	Fernando Mercado, Stuart Dattner TNRCC fmercado@tnrcc.state.tx.us sdattner@tnrcc.state.tx.us	March 2002	TNRCC Report Contribution to BRAVO final report, 2002 Conference presentation and/or journal article
A Review of Reconstructed Extinction	Bethany Georgoulias, Stuart Dattner, and others TNRCC bgeorgou@tnrcc.state.tx.us	March 2002	TNRCC Report Contribution to BRAVO final report, 2002 Conference and/or Journal

	sdattner@tnrcc.state.tx.us		
Multivariate and Mass Balance Analysis of Aerosol Data	Sonia Wharton, Erik Gribbin, Fernando Mercado, Stuart Dattner TNRCC swharton@tnrcc.state.tx.us egribbin@tnrcc.state.tx.us fmercado@tnrcc.state.tx.us	March 2002	TNRCC Report Contribution to BRAVO final report, 2002 Conference and/or Journal
Transport Analyses and Modeling			
Evaluate back trajectory methods and input wind fields	Kristi Gebhart NPS/CIRA 970 491-3684 gebhart@cira.colostate.edu	Winter 2002	Partial results in paper at A&WMA/AGU visibility conference, October 2001.
Empirical Orthogonal Function analysis of spatial and temporal patterns	Kristi Gebhart NPS/CIRA 970 491-3684 gebhart@cira.colostate.edu	Completed	Paper at A&WMA/AGU visibility conference, October 2001. Contribution to BRAVO final report, 2002.
Back trajectory regression method to estimate average source contributions to Big Bend	Kristi Gebhart NPS/CIRA 970 491-3684 gebhart@cira.colostate.edu	Winter 2002	Contribution to BRAVO final report, 2002.
Trajectory Analyses compared to Emissions Source Areas	Erik Gribbin, Sharon McDonald, Stuart Dattner TNRCC egribbin@tnrss.state.tx.us smcdonal@tnrcc.state.tx.us sdattner@tnrcc.state.tx.us	March 2002	TNRCC Report Contribution to BRAVO final report, 2002 Conference and/or Journal
HYSPLIT trajectories and influence functions for tracer source locations	Mark Green Desert Research Institute (LV) 702 895-0445 green@dri.edu	Completed	Presented on BRAVO conference call 11/16/00. Contribution to BRAVO final report, 2002.
TAGIT receptor modeling applied to tracer and sulfur data	Hampden Kuhns, Marc Pitchford, and Mark Green Desert Research Institute (LV) 702 895-0433 hkuhns@dri.edu	Fall 2001	Presented on BRAVO conference call 12/13/01. Submit manuscript to journal. Contribution to BRAVO final report, 2002.

Assemble modeling emissions inventory for states surrounding Big Bend in both the U.S. and Mexico	Hampden Kuhns Desert Research Institute (LV) 702 895-0433 hkuhns@dri.edu	Database complete. Report: September 2001	Paper at A&WMA/AGU visibility conference, October 2001. Section for BRAVO final report, 2002.
SCICHEM simulations to estimate power plant emissions contribution to sulfate at Big Bend	Naresh Kumar EPRI 650 855-2990 NKumar@epri.com	October 2001	Paper at A&WMA/AGU visibility conference, October 2001. Contribution to BRAVO final report, 2002
Backward air mass history analyses based on residence time	Bret Schichtel and Kristi Gebhart CIRA Colorado State University 970 491-8581 Schichtel@CIRA.colostate.edu	December 2001	Presented at BRAVO meeting in March 2001. Presentation at BRAVO meeting, Sept. 2001. Paper at A&WMA/AGU visibility conference, October 2001. Submit manuscript to journal. Contribution to BRAVO final report, 2002.
Forward air mass history analyses	Bret Schichtel and Kristi Gebhart CIRA Colorado State University 970 491-8581 Schichtel@CIRA.colostate.edu	March 2002	Presentation at BRAVO meeting, Sept. 2001. Paper at A&WMA/AGU visibility conference, October 2001. Submit manuscript to journal. Contribution to BRAVO final report, 2002.
Visualization of air mass transport	Bret Schichtel CIRA Colorado State University 970 491-8581 Schichtel@CIRA.colostate.edu	December 2001	Presented at BRAVO meeting in March 2001. Presentation at BRAVO meeting, September 2001.
Evaluation of Monte Carlo transport model and air mass history analysis techniques	Bret Schichtel CIRA Colorado State University 970 491-8581 Schichtel@CIRA.colostate.edu	December 2001	Presented at BRAVO meeting in March 2001. Presentation at BRAVO meeting, September 2001.
MM5 meteorological modeling. 36km and 12 km grid for entire study period. Also 4km grid for 8-17 October and 15-25 August 1999 episodes.	Nelson Seaman Department of Meteorology Pennsylvania State University 814 863-1583 seaman@ems.psu.edu	10/99 episode: Completed 8/99 episode: Dec. 2001 Remainder of study period: February 2002	Provide files to modelers as needed. Report (?)
Models-3/CMAQ simulations of 8-17 October and 15-25 August 1999	Christian Seigneur Atmospheric & Environmental	10/99 episode: January 2002	Paper on tracer simulation at A&WMA/AGU visibility conference, October 2001.

episodes	Research, Inc. 925 244-7121 Seigneur@aer.com	8/99 episode: March 2002	Report in 2002